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Optimization on Temperatures of Filament and Substrate for High-Quality Narrow Gap a-$Si_{1-x}Ge_x$:H Alloys Grown by Hot-Wire CVD

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Optimization of Filament and Substrate Temperatures for High-Quality Narrow-Gap a-$Si_{1-x}Ge_x$:H Alloys Grown by Hot-Wire CVD

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ABSTRACT

We improve narrow-bandgap ($1.2 < E_{Tauc} < 1.3$ eV) amorphous silicon germanium (a-$Si_{1-x}Ge_x$:H) alloys grown by hot-wire chemical vapor deposition (HWCVD) by lowering both substrate and filament temperatures. We grew two series of films using a tungsten filament. First we systematically varied the filament temperature (T_f) from our standard temperature of 2150°C down to 1750°C, while fixing all other deposition parameters. Secondly we systematically varied the substrate temperature (T_s) from our previous optimized temperature of 350°C down to 125°C, while fixing all other deposition parameters including T_f = 1800°C. Films with the best properties are grown with T_f < 1880°C and T_s between 200°-250°C. Improvement of the material properties are characterized by improvements in the H-bonding, reduced microvoid density, and good photoresponse (for a given E_{Tauc}). There are about 15% more Ge-H bonds—passivating Ge-dangling bonds—relative to our previous work. The films are more compact due to microvoid reduction as measured by small-angle X-ray scattering (SAXS). We also fabricated solar cells with these optimized materials and obtained ~3.58%-efficient devices without doing bandgap profiling yet. Due to the high optical absorption of these a-$Si_{1-x}Ge_x$:H (~1.25 eV bandgap) alloys, we need an i-layer that is only ~1200 Å thick to obtain a J_{sc} of ~20 mA/cm^2. Additionally, we increased the GeH_4 gas utilization relative to SiH_4 from previous work, which was about 1:1 (GeH_4 in gas to Ge in film). Under the current conditions, a 35% GeH_4 gas fraction produces an a-$Si_{1-x}Ge_x$:H film with x = 0.7.

Introduction

It is well known that a-$Si_{1-x}Ge_x$:H alloys are essential for the fabrication of multijunction solar cells. The world-record cell (14.6% initial efficiency) was made by USSC using these alloys as the middle and bottom cells [1]. Our early attempts to grow "device quality" a-$Si_{1-x}Ge_x$:H with bandaps below 1.5 eV by HWCVD had limited success [2]. Those films were grown under conditions that give "device quality" a-Si:H, namely, high T_f and T_s. By decreasing both T_f and T_s, as well as reducing our filament diameter from 0.5 mm to 0.38 mm, we now grow films with optoelectronic properties equal to films grown by PE CVD [3].

Experiment

All the samples used in this paper are grown in a HWCVD tube reactor [3]. The main deposition parameters for the two series grown for this study are in Table 1.

Table 1: Summary of Main Deposition Parameters

Sample (Set 1)	T_f (°C)	T_s (start) (°C)	Thick. (Å)	R_d (Å/s)
L902	2150	180	2976	9.92
L904	2065	180	3434	8.18
L905	1975	180	3315	6.50
L907	1880	180	2997	4.16
L911	1800	180	2128	2.03
L913	1750	180	2085	0.98
L908	1800	350	2919	3.04
L894	1800	300	4087	3.45
L895	1800	250	3669	3.08
L896	1800	200	3622	2.92
L897	1800	150	3501	2.84
L898	1800	125	2856	2.14

We deposited each sample simultaneously on a 2.5-cm x 2.5-cm 1737F Corning glass substrate and a 2.5-cm x 1.5-cm c-Si wafer. We evaporated coplanar (width to length = 0.05) Cr contacts on the films on the 1737F substrates for conductivity measurements using a Keithley model 6517a electrometer. The photoconductivity is measured under an ELH lamp set to approximate an AM1.5 solar spectrum. We perform UV/Visible optical spectroscopy using an n&k 1280 analyzer on the films grown on 1737F substrates to determine the thickness, bandgap, refractive index (n), and the extinction coefficient (k). Note that this instrument readily calculates an E04 gap, that is, the photon energy where the optical absorption is 10^4. The Tauc bandgap is taken from the fitting of E vs. $(\alpha h\upsilon)^{1/2}$, in which α is calculated by the method of interference-free determination of optical absorption coefficient on the raw data of transmission and reflectance from this spectrometer [4]. We use the films deposited on the c-Si for two structural measurements. We use Fourier transform infrared spectroscopy (FTIR) to calculate the hydrogen content (C_H), and study the hydrogen-bonding configuration to Si and Ge. We use secondary-ion mass spectroscopy (SIMS) to determine the Ge solid fraction (x) in the films.

For SAXS measurements, we duplicate the growth conditions from Table 1 in separate runs and deposit on high-purity aluminum foil. The total integrated SAXS intensity, Q_T, is a good measure of the overall film heterogeneity. The SAXS technique and analysis methods are described elsewhere [5].

Results and Discussion

1. *FTIR Results*

In Fig. 1, we display the FTIR spectra between 1700 and 2200 cm^{-1}, along with the superpositions of Gaussian fits to these spectra, for both film series. The absorption peaks for Ge-H, Ge-H_2, Si-H, and Si-H_2 bonding configurations are 1880, 1980, 2000, and 2090 cm^{-1}, respectively [6]. Because dihydride bonding (Ge-H_2 and Si-H_2) is deleterious to film quality, the best films are grown with T_f < 1880°C and T_s between 200-250°C. This assertion is consistent with photoconductivity and photoresponse data to be presented with additional analysis at the upcoming MRS meeting [7].

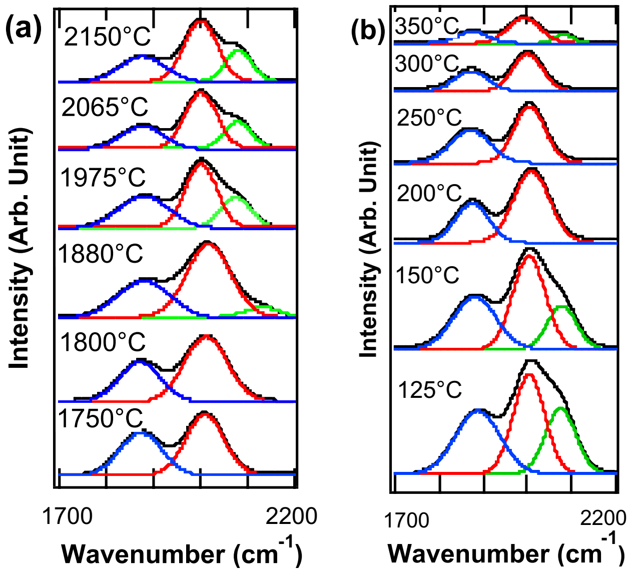

Figure 1: FTIR bonding configurations for the T_f series (a) and the T_s series (b).

2. *SAXS and SIMS Results*

In Fig. 2, we display both the total integrated SAXS intensity (Q_T) and the x as measured by SIMS, for both film series. There is a monotonic decrease in film heterogeneity (probably a decrease in microvoid density) as well as an increase in the germanium content of the films as the filament temperature is lowered from 2150° to 1750°C (Fig. 2a). There is a clear minimum in Q_T for the T_s series, centered at 220°C, whereas there is a decrease in x for increasing T_s. This minimum in Q_T correlates with the minimum in the dihydride bonding in the films, supporting the interpretation that –H_2 bonding occurs on void surfaces; as the heterogeneity increases, the –H_2 bonding increases.

Conclusions

We improved narrow-gap (1.2 < E_g<1.3 eV) a-$Si_{1-x}Ge_x$:H alloys by optimizing T_f and T_s to reduce the dihydride bonding in the films and thus improve their optoelectronic properties. These materials are device quality, and further work is necessary to implement them in bandgap-graded device structures. Additionally, we will quantify the effect of deposition rate on film quality due to process changes.

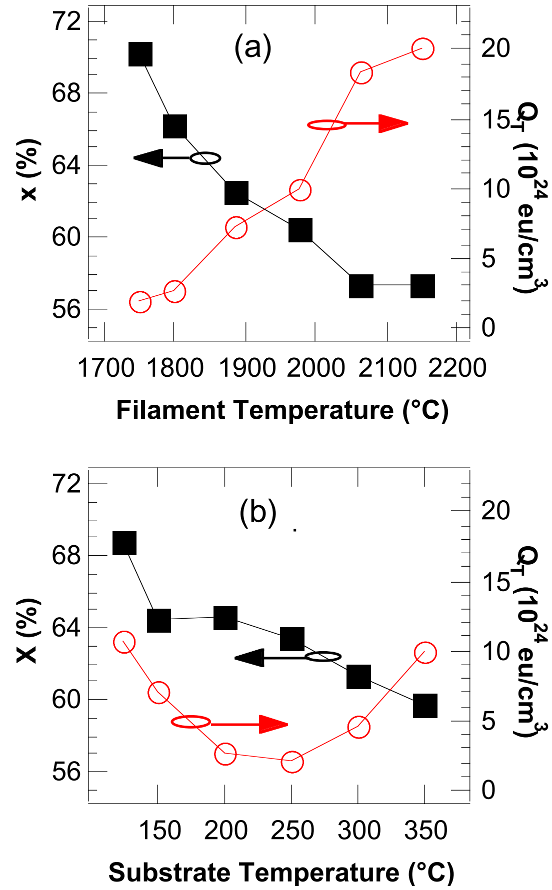

Figure 2: Ge fraction in the film by SIMS (x, left axis) and total integrated SAXS intensity (Q_T, right axis) for the T_f series (a) and the T_s series (b).

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